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(57) Abstract

The invention provides compositions and methods for imparting translucent optical effects to transparent thermoplastic polymers. The compositions comprise the polymer and 0.01 to 10 parts per hundred by weight of a particulate, light-scattering material comprising an average particle diameter of from about 0.1 microns to about 200 microns. The particulate material may be organic or inorganic and be in the form of powders, flakes, platelets, fibers, whiskers, and mixtures of these. The translucent optical effects are obtainable in a continuum of very smooth to very grainy, depending on the type and concentration of the particles employed.

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TITLE OF THE INVENTION

CONCENTRATE COMPOSITIONS FOR IMPARTING A TRANSLUCENT OPTICAL EFFECT TO TRANSPARENT THERMOPLASTIC POLYMERS

CONCENTRATE COMPOSITIONS FOR IMPARTING A TRANSLUCENT OPTICAL EFFECT TO TRANSPARENT THERMOPLASTIC POLYMERS

BACKGROUND OF THE INVENTION

Transparent thermoplastic polymers are widely used in place of glass in the manufacture of a variety of products because of their light weight, their resemblance to glass, their economical use, and their excellent impact resistance and other physical properties. For example, transparent blow-molded containers, such as vials, cosmetic bottles, liquid flavoring containers and beverage bottles made of polyethylene terephthalate (PET), are increasingly in demand because they are easily molded and relatively inexpensive. Transparent thermoplastic polymers are used for a variety of other molded, extruded or formed products, such as drinking cups, cooking and eating utensils, food containers, refrigerator storage containers, medical and pharmaceutical tubing and extruded parts, packaging films, extruded sheets and toys. In addition to PET, the transparent polymers commonly used in the manufacture of these products include, for example, styrene acrylonitrile copolymers (SAN), polycarbonates, acrylics, ionomers, polystyrenes, and the like.

Although most transparent plastics have excellent clarity and resemblance to glass, it is desirable in many cases to improve the aesthetic appearance of transparent plastic products by making them translucent, i.e. "frosted". In the context of the invention, the terms "translucent" and "frosted" are intended to encompass all gradations of translucency, from almost transparent to almost opaque. Such treatment is intended to impart a softer, more elegant and high grade visual textured appearance to the plastic. Containers and other products having a frosted glass appearance are in demand particularly in the packaging of cosmetics, health, beauty and personal hygiene

goods, foods and beverages, as well as for household products, such as frozen food trays, tableware (dishes, cups, plates) and other decorative and utilitarian housewares, and other products, such as overhead lighting diffusers and cigarette lighters. The frosted glass appearance can be visual only (a smooth surface) or can be both visual and tactile (a rough surface).

Conventional methods for making transparent plastic products translucent include spraying the smooth outer surface of the plastic product with a coating to form a matte surface layer. The plastic article appears frosted because the rough surface diffusely reflects light. Such matte coatings, however, tend to be easily separated from or scratched off the smooth polymer surface due to friction with other articles, and they require an extra production step which adds to production costs. Another method employs a mold with an inner surface that has been roughened to impart a rough or textured matte finish to the molded product. However, the roughened mold may be more expensive to manufacture than a standard mold and, because it is permanent, the mold is limited to producing finished products having a matte surface. Moreover, rough matte surfaces that are designed to resemble ground or frosted glass have tiny projections and recesses that reflect light but may be unpleasant to the touch and easily soiled due to dust and oils transferred from the hands. Oils, in particular, fill recesses and add shine to these rough surfaces. Thus, the amount of the amount of diffused light is decreased and any original lustrous appearance may be readily lost.

Other reported methods for achieving a frosted effect in blow-molded bottles and other containers include injection molding of a preformed piece, followed by sandblasting and then heat-crystallizing of the outer surface to roughen and opacify the surface layer prior to the blow molding step. A ground glass effect has been produced in plastic containers by using a blend of olefin resins in which one resin comprises a continuous phase in which another resin is dispersed. Frosted surfaces on bottles have been achieved by heat-

crystallizing the outer surface while leaving the inner surface transparent, to form a milky white or translucent effect. Chemical flatting agents have also been employed to opacify acrylic.

Although the above methods produce various types of frosted glass effects, there is still a need for simple and inexpensive methods and compositions for imparting a translucent frosted glass effect to transparent thermoplastic polymers.

SUMMARY OF THE INVENTION

The invention provides inexpensive compositions and one-step and two-step methods for imparting a variety of individual translucent optical effects to transparent thermoplastic polymers. The methods and compositions of the invention are particularly useful for imparting a lustrous and rich translucent optical effect to packaging products, such as blow-molded and injection molded products manufactured from polyethylene terephthalate (PET) and styrene acrylonitrile copolymer (SAN), which have traditionally been left transparent because of their excellent clarity and resemblance to glass. Although the invention is herein described with respect to transparent polymers, a translucent effect may also be obtained by the compositions and methods of the invention in polymers that are "near transparent", such as high density polyethylene and polypropylene. The term "transparent", as used herein below, is intended to encompass all grades of thermoplastic polymers that are "near transparent" as well as transparent.

The desired translucent optical effect is selectable from a continuum of visual effects from very smooth to very grainy, and is accomplished by selecting an appropriate invention composition and method. Transparent or semitransparent color compounds, pigments and dyes may also be added to the invention compositions to produce colored translucent products.

The invention employs conventional molding, extruding and forming techniques with existing tooling. Thus, the methods do not require expensive extra production steps; nor do they require specialized tools. By the method, a translucent visual frosted glass effect can be imparted to virtually any transparent or near transparent thermoplastic polymer used in the production of molded, extruded or formed products, including films.

In one embodiment of the invention, a one-step method comprises forming a composition comprising (i) 0.01 to 10 parts by weight of a particulate, light-scattering material having an average particle diameter of about 0.1 micron to about 200 microns, preferably about 1 micron to about 100 microns, and (ii) 90 to 99.99 parts by weight of a transparent thermoplastic polymer. The mixture may be molded, extruded or formed by conventional means to form a translucent polymer product.

The particulate material may be in the form of, for example, powders, flakes, platelets, fibers, whiskers, and mixtures of these. Preferably, the particulate material is selected from the group consisting essentially of calcium carbonates, calcium sulfates, talc, silicates, kaolin, silicas, mica flakes, mica platelets, mica pearls, titanates, metal sulfates, metal carbonates, sulfides, metal oxides, borides, wollastonite, basalt, boron, ceramics, single crystal fibers, organic flatting agents, acrylic flatting agents, fiber organic resins, ground organic resins, and mixtures of the foregoing.

In another embodiment of the invention, a two-step method is employed that comprises the steps of forming a concentrate composition which comprises a mixture of (i) 40 to 90 parts by weight of a carrier agent selected from the group consisting essentially of a first transparent thermoplastic polymer, a dispersing agent, and mixtures of these, and (ii) 10 to 60 parts by weight of the particulate, light-scattering material having an average particle size of about 0.1 to 200 microns, preferably about 1 to about 100 microns, as described above. If a mixture of the first polymer and the dispersing agent is

employed, the mixture preferably comprises 80 to 98 parts by weight of the first polymer and 2 to 20 parts by weight of the dispersing agent. The carrier agent is preferably finely ground, finely flaked or finely pelletized and, more preferably is finely ground. The concentrate, in an amount of 0.1 to 10 parts by weight, is then mixed with 90 to 99.9 parts by weight of a second transparent thermoplastic polymer that is chemically compatible with the carrier agent, to form a second mixture which is then molded, extruded or formed by conventional means to form the translucent polymer product. The method may optionally include a further step in which the concentrate is extruded and pelletized before adding it to the second polymer.

By either the one-step method or the two-step method, the resulting translucent polymer product comprises 0.01 to 10 parts by weight of the particulate material and exhibits an average translucency having a contrast ratio, at a molded part thickness of 0.030 inches, of about 2% to about 20% higher than the contrast ratio of a polymer part comprising the polymer alone.

DETAILED DESCRIPTION OF THE INVENTION

A translucent frosted glass effect in transparent thermoplastic molded, extruded or formed polymer products is obtained by the methods and compositions of the invention. The compositions and methods may be employed to impart a translucent optical effect to virtually any transparent or near transparent grade of thermoplastic polymer including, but not limited to, polyolefins, polyethylene terephthalate, glycol-modified polyethylene terephthalate, glycol-modified polycyclohexane-methanol terephthalate, acid-modified polycyclohexanemethanol terephthalate, polystyrene, styrene acrylonitrile copolymers, styrene butadiene, styrene acrylic ester, acrylonitrile butadiene styrene, acrylonitrile styrene acrylic ester, acrylics, polymethacrylonitrile, ethylene methylacrylate, polymethylmethacrylate, ethylene ethylacrylate, ethylene butylacrylate, ethylene acrylic ester, cellulose

butyrate, polymethylpentene, polyisobutene, polybutene, polyamides, polycarbonate, ionomers, polyurethane, liquid crystal polymers, cellulose propionate, polyvinyl alcohol, ethylene vinyl alcohol, ethylene vinylacetate copolymer, polyvinyl chloride, high density polyethylene, polypropylene, polyacetal, and copolymers, grafts and blends of the foregoing.

The frosted glass effect may be a visual effect only, such as that obtained when a composition of the invention is extruded, formed, or produced in a mold having a smooth surface, to produce a smooth-surfaced translucent product. Alternatively, the effect may be both visual and tactile, such as that obtained by molding the composition of the invention in a mold having a textured surface to impart a matte finish to the translucent product. As described further below, transparent or semitransparent color concentrates, pigments or dyes may also be blended with the invention compositions to produce colored translucent products, such as a "pink frost", a "green frost", a "lavender frost" etc., in addition to a "clear" or "natural" frosted product. Suitable organic pigments, inorganic pigments and polymer-compatible dyes are known to those skilled in the art of making colored polymers.

The translucent optical effects imparted by the compositions and methods of the invention are achieved by mixing very small quantities of light-scattering particles, having a particle diameter of about 0.1 to about 200 microns, preferably about 1 to about 100 microns, with a transparent thermoplastic polymer prior to molding or extruding the mixture. Preferably, the particles are selected on the basis of their ability to reflect and transmit light diffusely, rather than rectilinearly or specularly, and the translucent visual effect more closely resembles a matte finished molded or spray-coated product. Thus, for example, light-diffusing materials, such as non-shiny mica particles used for laser marking, are preferred over light reflecting (specular) materials, such as mica pearls. However, mica pearls may also be employed to achieve a frosted effect with a more "satin" appearance.

To achieve the desired frosted effect, the light scattering particles may be in any form, such as powders, fibers, whiskers, platelets, flakes, or mixtures of these. Suitable particles include, but are not limited to, calcium carbonates, such as ground chalk, ground limestone, ground marble and ground dolomite; ground or fiber calcium sulfates; silicates, such as glass fibers, glass flakes, solid and hollow glass spheres, aluminum silicate, synthetic calcium silicate and zirconium silicate; talc; kaolin; mica flakes, platelets and pearls; natural silicas, such as sand, quartz, quartzite, perlite, tripoli and diatomaceous earth; fumed silicas; titanates, such as barium titanate; sulfates, such as barium sulfate; sulfides, such as zinc sulfide and molybdenum sulfide; metallic oxides, such as aluminum oxide, zinc oxide, beryllium oxide, magnesium oxide, zirconium oxide, antimony oxide, titanium dioxide and aluminum hydroxide; aluminum diboride flakes; inorganic fibers, such as wollastonite, basalt, boron and ceramic; single crystal fibers (i.e. whiskers), such as those of alumina trihydrate; short fibers, such as those of aluminum silicate with aluminum and magnesium oxides and calcium sulfate hemihydrate; organic flatting agents, such as wood flour and starch; acrylic flatting agents; fiber and ground organic resins, such as polyester, polyvinyl alcohol, polyethylene terephthalate, and aromatic polyamide fibers; and mixtures of any of the foregoing.

A desired translucent optical effect ranging in a continuum from very smooth visual textured effects to very grainy visual textured effects may be achieved, depending on the particulate material or mixture of particulate materials selected and the quantity of the particulate employed. For example, a smooth visual translucency is obtained by using white powder particulates, such as barium sulfate, zinc sulfide, ultrafine ground chalk or acrylic flatting agents. Slightly grainy visual translucency is obtained by using transparent particulates, such as solid glass microspheres having a particle diameter of about 2 to about 100 microns (preferably about 4 to about 44 microns) or hollow glass microspheres having a particle diameter of about 10 to 100

microns (preferably about 65 to about 75 microns); whereas a slightly more grainy visual translucency is obtained by using ceramic fibers having a diameter of about 2 to about 12 microns, and lengths of about 45 microns to about 1.5 millimeters (mm). Grainy translucent visual effects are also obtained with additives such as lamellar kaolin having an aspect ratio of 10:1 (length:diameter). To obtain very grainy visual translucent effects, wollastonite having aspect ratios ranging from about 5:1 to 15:1, are employed, with the highest aspect ratios giving the grainiest effects. Very grainy translucent visual effects are also achieved by using whiskers, such as such as those of alumina trihydrate, and metal flakes or platelets, such as those of mica.

Exemplary suitable particles for use in the invention are Zeeospheres W-610 (ceramic microspheres, mixture of particle sizes of approximately 2 to 45 microns, Zeelan Industries, St. Paul, MN); Silcron G602 (fine particle silica, average particle size approximately 2.7 microns, SCM Pigments, Baltimore, MD); NYAD G Wollastocoate (wollastonite, aspect ratio 15:1, 100-325 mesh), NYAD 400 wollastonite (aspect ratio 5:1), 400 Wollastocoate (aspect ratio 5:1, 400 mesh) (NYCO Minerals, Inc., Willsboro, NY); hollow glass microspheres (glass bubbles, 3M Corporation); Paraloid EXL-5137 (acrylic flatting agent, approximately 30 mesh, Rohm and Haas); Acematt TS100 (silica flatting agent, average particle size approximately 2 to 10 microns, Degussa Corp., Ridgefield Park, NJ); and Iriodin/Lazer Flair LS 810 (mica-based additive, particle size approximately 2 to 28 microns, EM Industries, Hawthorne, NY).

Because the quantities of the particulates employed in the invention compositions and methods are extremely small, the particulates do not perform the traditional functions of fillers (e.g. reinforcers, extenders, opacifiers, plasticizers, etc.).

In one embodiment of the invention, a one-step method for imparting a translucent optical effect to a transparent thermoplastic polymer is

employed, and comprises the steps of forming a substantially homogeneous composition comprising a mixture of (i) 0.01 to 10 parts by weight of a particulate, light-scattering material having an average particle diameter of from about 0.1 microns to about 200 microns, and (ii) 90 to 99.9 parts by weight of a transparent thermoplastic polymer; and molding, extruding or forming the homogeneous mixture to form a translucent molded, extruded or formed polymer product. Preferably the particles have an average diameter of from about 1 to about 100 microns. Preferably, the mixture comprises 0.1 to 6 parts by weight of the particulate material and, more preferably, 1 to 4 parts by weight of the particulate material.

In this embodiment of the invention, to achieve a substantially homogeneous mixture of the particulates and the polymer for a homogeneous translucent optical effect, it is preferred that the pelletized polymer be finely ground to a 20-mesh powder, prior to mixing with the particulates. As discussed further below, a dispersing agent and/or a flow enhancing (anti-bridging) agent may also be added to the particulate mixture to aid in achieving homogeneity. For practical purposes, when mixing large amounts of polymer with particulates, the polymer is not pre-ground to a powder but may be used in commercially available pellet form (average diameter 1/16 inch to 1/8 inch or greater). The achievable homogeneity of a pelleted polymer/particulate mixture, however, depends upon such factors as the type of particulate employed, the pellet and particulate diameter, the mixing time, the natural segregation of the components during the time period before use, and the like, resulting in a product which may have a variable, rather than a homogeneous, overall translucent appearance. Thus, this embodiment of the composition and method is less preferred if a high degree of homogeneity of the optical effect is desired. Homogeneity of a pelleted polymer/particulate mixture may be improved by separately metering the polymer pellets and the particulates (frosting agents, and/or dispersants and/or flow enhancers) through separate

feed lines into the melting screw portion of any device used during the melt mixing phase of the extruding, molding or forming process.

In another embodiment of the invention, a two-step method is employed. By this method, a substantially homogeneous concentrate mixture comprising the particulate material in a carrier agent is prepared. A desired quantity of this concentrate is then blended with a chemically compatible polymer (let down resin) to form a second mixture, which is then molded, extruded or formed and cured, as described above, to form the translucent polymer product. The degree of translucency can be adjusted by increasing or decreasing the loading (i.e. the "let down ratio" of concentrate to let down resin) of the concentrate in the end product.

The two-step method comprises the steps of forming a concentrate composition comprising a mixture of (i) 40 to 90 parts by weight of a finely ground, finely flaked or finely pelletized carrier agent, selected from the group consisting essentially of a first transparent thermoplastic polymer, a dispersing agent, or mixtures of these, and (ii) 10 to 60 parts by weight of the particulate, light-scattering material described above, to form a second mixture that comprises 0.1 to 10 parts by weight of the composition and 90 to 99.9 parts by weight of a second transparent thermoplastic polymer that is chemically compatible with the carrier agent. The dispersing agent comprises a low molecular weight substantially transparent polymeric material, such as a silicone wax, a fatty acid, a metallic salt, an ionomer wax, an amide wax, a hydroxy stearate, an olefinic wax, or a mixture of any of the foregoing, and is preferably a bis-stearamide or a hydroxy stearate.

The concentrate and second polymer may be combined in a process during the melt mixing phase, such as by their separate metering into the melting screw portion of the device through separate feed lines. Alternatively, the concentrate and the second polymer may be mechanically combined prior to the introduction of the mixture into a molder or extruder.

The mixture is then molded or extruded to form a translucent polymer product.

The carrier agent may comprise any agent that is capable of forming a substantially homogeneous dispersion therein of the particulate material. The carrier agent may comprise finely ground (e.g. 20 mesh) polymer pellets or a finely ground or finely flaked dispersing agent, such as a silicone wax, fatty acid, metallic salt, ionomer wax, amide wax, hydroxy stearate, olefinic wax, or a mixture of any of these. Exemplary dispersing agents comprise a bis-stearamide, such as ethylene-bis-stearamide, or a hydroxy stearate, such as Castorwax (Caschem, Bayonne, NJ). To prepare finely ground polymer pellets, commercially available polymer pellets are ground by conventional methods, such as in an ambient or cryogenic grinder, to about a 20-mesh powder. Fine flaking of the wax-base dispersing agent is achieved by known methods to form flakes that are typically irregular or uneven and preferably have a maximum dimension of 1/4 inch.

Optionally, when the finely ground polymer is employed as the carrier agent, 0 to 20 parts per weight of a dispersing agent and/or 0.1 to 7 parts, preferably 1 to 2 parts, of a flow enhancing or anti-bridging agent, such as fumed or precipitated silica, may be added to the mixture. One to 2 parts by weight of a flow enhancing agent may also be added to the mixture when a dispersing agent is employed as the carrier agent. Other additives, known to those skilled in the art of polymer compounding, may include anti-oxidants, UV absorbers/light stabilizers, and the like, in quantities that do not contribute substantially to or interfere with the translucent optical effect. In addition, transparent or semi-transparent colorants, pigments and dyes may be added to the mixture to provide colored translucent products.

For purposes of this invention, a translucent optical effect is defined by a measurement of the translucency of the polymer product, after curing, by its contrast ratio. The contrast ratio is the ratio of the percent reflectance of a sample over a white background and the percent reflectance of

the sample over a black background. Contrast ratios from 0 to 100 are obtainable, with samples having ratios of greater than 97 being considered opaque. When different samples are measured over the same white and black backgrounds, contrast ratios may be used for comparison of the relative degrees of opacity between samples. The polymer product formed by either the one-step method or the two-step method described above comprises 0.01 to 10 parts by weight of the particulate material and exhibits, after curing, an average translucency having a contrast ratio that is about 2% to about 60% higher than the contrast ratio of a polymer part comprising the polymer alone, at a molded part thickness of 0.030 inches.

The following examples are illustrative of the methods and compositions of the invention for imparting translucent effects to transparent thermoplastic polymers. The examples are not intended to be limiting, as other polymers, carrier agents, dispersing agents, flow enhancing agents, particulate materials, colorants, and other additives may be used in other quantities and combinations, without departing from the scope of the invention.

Examples 1-9:

The formulations of each of nine concentrate compositions are listed in **Table 1**. Ground PET (20 mesh) is prepared by grinding commercially available PET pellets at ambient temperature. For each of the formulations, the ingredients are mixed in a Henschel mixer to obtain a uniform blend (about one to two minutes). The blend is then fed into an extruder and strand pelletized to form concentrate pellets, preferably miniature concentrate pellets having a diameter of 1/16 inch or less. The concentrate pellets are then ready for use in any injection molding, blow molding, extruding or forming process and are added to a compatible let down resin in the let down ratios (resin to concentrate) described in the Table.

Examples 10-20:

Measurements are made of the translucency of blow-molded PET bottles having the formulations illustrated in **Table 2** and manufactured from "natural frost" PET concentrates with let down ratios of 25:1. Test sample 13 comprises PET only, without particulate additives to obtain translucency. Samples 14-20 comprise PET and particulate additives, as shown. The "gloss" at 60° of samples 14-20 is significantly reduced when compared to sample 13 containing no particulate additives.

Contact clarity is a visual rating of clarity when looking through a sample at a black line on a piece of paper that is in contact with the back of the sample. Samples 14-16 and 20, comprising a combination of wollastonite and/or zeeosphere particulates, have less contact clarity than samples 17-19 comprising a single particulate additive.

Although the samples are a "natural" frost, they demonstrate a bluish or yellowish under tone or top tone, depending on the type of particulate additive employed, due to a degree of color tone imparted to the polymer by the additive.

Each of the samples 14-20 are translucent, and therefore slightly more opaque than sample 13 comprising PET alone. Contrast ratios of samples 14-20 are between 9% and 45% higher than that of sample 13 comprising PET alone, with the samples containing individual additives having the lowest contrast ratios, and thus the lowest opacities.

While the invention has been described herein with reference to the preferred embodiments, it is to be understood that it is not intended to limit the invention to the specific forms disclosed. On the contrary, it is intended to cover all modifications and alternative forms falling within the spirit and scope of the invention.

Table 1
(Examples 1-9)

1. **Natural Frost Concentrate for PET**

Ground PET (.75 IV)*	50%
Barium Sulfate	50%
Let Down Ratio**	66.7:1

2. **Black Frost Concentrate for PET**

Ground PET (.8 IV)	66.86%
Barium Sulfate	31.78%
Channel Carbon Black	0.34%
Phthalocyanin Blue†	0.02%
Castorwax	1.00%
Let Down Ratio	25:1

3. **Natural Frost Concentrate for PET**

Ground PET	50%
Wollastonite‡	50%
Let Down Ratio	25:1

4. **Natural Frost Concentrate for PET**

Ground PET	50%
Hollow Glass Bubbles	50%
Let Down Ratio	25:1

5. **Natural Frost Concentrate for PET**

Ground PET	75%
Silcron G602	25%
Let Down Ratio	25:1

Table 1 (cont'd)

6. **Natural Frost Concentrate for PET**

Castorwax	30%
Zeeospheres W610	10%
Nyad G Wollastonite	30%
Nyad 400 Wollastonite	30%
Let Down Ratio	20:1

7. **Natural Frost Concentrate for PET**

Ground PET	49.6%
Castorwax	3.0%
Zeeospheres W610	6.8%
Nyad G Wollastonite	20.3%
Nyad 400 Wollastonite	20.3%
Let Down Ratio	12.5:1

8. **Natural Frost Concentrate for PET**

Pellet PET	75%
Paraloid EXL-5136	25%
Let Down Ratio	20:1

9. **Natural Frost Concentrate for PET**

Ground PET	75%
Zeeospheres W610	25%
Let Down Ratio	20:1

* "IV" is the intrinsic viscosity of the grade of the polyethylene terephthalate (PET) employed.

** The ratio of the let down resin to the concentrate in the final composition suitable for molding, extruding or forming the final polymer product.

† An organic pigment.

‡ Any of Nyad 400 (aspect ratio 5:1), Nyad G (aspect ratio 15:1), or 400 Wollastocoate (aspect ratio 5:1), or mixtures of these, may be used.

TABLE 2

Sample Number	Formula[1] G	400	W610	PET	Gloss[2] 60°	20°	85°	Contact[3] Clarity	Under[4] Tone	Top[5] Tone	Contrast[6] Ratio
Baseline[7]											
10	1.5	1.5	0.5	96.5	97.6	87.5	97.1	3	N		20.27
11	1.5	1.5	0.5	96.5	97.0	87.2	97.7	3	N		20.35
12	1.5	1.5	0.5	96.5	99.1	89.7	99.1	4	N		20.99
Test											
13	0	0	0	100.0	139.4	141.5		1	-		16.66
14	3	0	1	96.0	99.3			4	N		21.33
15	0	3	1	96.0	98.2			4	N		22.36
16	3	3	0	96.0	95.7			4	Bluest	Y	21.23
17	0	0	1	96.0	100.9			3	Yellowest		18.90
18	3	0	0	96.0	101.9			2	B	Y	18.29
19	0	3	0	96.0	100.1			2	B	Y	19.28
20	3	3	1	96.0	94.9			5	N		24.15

Table 2 (cont'd)

[1] Formulations are given as percentages of polymer and additives. G = Nyad G Wollastonite; 400 = Nyad 400 Wollastonite; W610 = Zeeospheres; PET = ground (20 mesh) polyethylene terephthalate.

[2] Degrees refer to the angle of the sample relative to the measuring device. It is know that gloss measurements should be less than 100. These data should therefore be considered relative comparisons.

[3] A visual measure of opacity. 1 = Clear; higher numbers indicate more opaque.

N = neutral color; B = blue; Y = Yellow; - = not applicable

[4] Under tone: the visual color tone of the sample when light is transmitted through it.

[5] Top tone: the visual color tone of the exterior of the sample.

[6] A measure of opacity. A higher number indicates more opaque.

[7] Baseline data for samples 10-13 illustrates the reproducibility of the tests. Test data is for each concentrate test sample 14-10.

I claim:

1. A composition for imparting a translucent optical effect to a transparent thermoplastic polymer, comprising:

   (i) 0.01 to 10 parts by weight of a particulate, light-scattering material comprising an average particle diameter of from about 0.1 microns to about 200 microns, and

   (ii) 90 to 99.99 parts by weight of a transparent thermoplastic polymer.

2. The composition of claim 1, wherein the particulate material comprises an average particle diameter of from about 1 micron to about 100 microns.

3. The composition of claim 1, wherein the particulate material comprises 0.1 to 6 parts by weight.

4. The composition of claim 1, wherein the particulate material comprises 1 to 4 parts by weight.

5. The composition of claim 1, wherein the particulate material is selected from the group consisting essentially of calcium carbonates, calcium sulfates, talc, silicates, kaolin, silicas, mica flakes, mica platelets, mica pearls, titanates, metal sulfates, metal carbonates, sulfides, metal oxides, borides, wollastonite, basalt, boron, ceramics, single crystal fibers, organic flatting agents, acrylic flatting agents, fiber organic resins, ground organic resins, and mixtures thereof.

6. The composition of claim 1, wherein the polymer is selected from the group of transparent and near transparent grades of thermoplastic polymers consisting essentially of polyolefins, polyethylene terephthalate, glycol-modified polyethylene terephthalate, glycol-modified polycyclo-hexanemethanol terephthalate, acid-modified polycyclo-hexanemethanol terephthalate, polystyrene, styrene acrylonitrile copolymers, styrene butadiene, styrene acrylic ester, acrylonitrile butadiene styrene, acrylo-nitrile styrene acrylic ester, acrylics, polymethacrylo-nitrile, ethylene methylacrylate, polymethylmethacrylate, ethylene ethylacrylate, ethylene butylacrylate, ethylene acrylic ester, cellulose butyrate, polymethylpentene, polyisobutene, polybutene, polyamides, polycarbonate, ionomers, polyurethane, liquid crystal polymers, cellulose propionate, polyvinyl alcohol, ethylene vinyl alcohol, ethylene vinylacetate copolymer, polyvinyl chloride, high density polyethylene, polypropylene, polyacetal, and copolymers, grafts and blends thereof.

7. A composition for imparting a translucent optical effect to a transparent thermoplastic polymer, comprising:

0.1 to 10 parts by weight of a mixture that comprises

(i) 40 to 90 parts by weight of a finely ground, finely flaked or finely pelletized carrier agent selected from the group consisting essentially of a first transparent thermoplastic polymer, a dispersing agent, and mixtures thereof, wherein the dispersing agent is selected from the group consisting essentially of silicone waxes, fatty acids, metallic salts, ionomer waxes, amide waxes, hydroxy stearates, olefinic waxes, and mixtures thereof; and

(ii) 10 to 60 parts by weight of a particulate, light-scattering material having an average particle diameter of from about 0.1 microns to about 200 microns;

and 90 to 99.9 parts by weight of a second transparent polymer that is chemically compatible with the carrier agent.

8. The composition of claim 7, wherein the particulate material comprises an average particle diameter of from about 1 micron to about 100 microns.

9. The composition of claim 7, wherein the carrier agent comprises a mixture of 80 to 98 parts by weight of the first polymer and 2 to 20 parts by weight of the dispersing agent.

10. The composition of claim 7, wherein the carrier agent comprises a bis-stearamide compound.

11. The composition of claim 7, wherein the carrier agent comprises a hydroxy stearate.

12. The composition of claim 7, wherein the homogeneous mixture further comprises 0.1 to 7 parts by weight of a flow enhancing compound.

13. The composition of claim 12, wherein the flow enhancing compound is selected from the group consisting essentially of fumed silica, precipitated silica, and mixtures thereof.

14. The composition of claim 7, wherein the first and second polymers are the same or different and are independently selected from

the group of transparent and near transparent grades of thermoplastic polymers consisting essentially of polyolefins, polyethylene terephthalate, glycol-modified polyethylene terephthalate, glycol-modified polycyclohexanemethanol terephthalate, acid-modified polycyclohexanemethanol terephthalate, polystyrene, styrene acrylonitrile copolymers, styrene butadiene, styrene acrylic ester, acrylonitrile butadiene styrene, acrylonitrile styrene acrylic ester, acrylics, polymethacrylonitrile, ethylene methylacrylate, polymethyl-methacrylate, ethylene ethylacrylate, ethylene acrylic ester, ethylene butylacrylate, cellulose butyrate, polymethylpentene, polyisobutene, polybutene, polyamides, polycarbonate, ionomers, polyurethane, liquid crystal polymers, cellulose propionate, polyvinyl alcohol, ethylene vinyl alcohol, ethylene vinylacetate copolymer, polyvinyl chloride, high density polyethylene, polypropylene, polyacetal, and copolymers, grafts and blends thereof.

15. The composition of claim 7, wherein the particulate material is selected from the group consisting essentially of calcium carbonates, calcium sulfates, talc, silicates, kaolin, silicas, mica flakes, mica platelets, mica pearls, titanates, metal sulfates, metal carbonates, sulfides, metal oxides, borides, wollastonite, basalt, boron, ceramics, single crystal fibers, organic flatting agents, acrylic flatting agents, fiber organic resins, ground organic resins, and mixtures thereof.

16. A molded, extruded or formed polymer product having a translucent optical appearance, comprising:

(i) 0.01 to 10 parts by weight of a particulate, light-scattering material comprising an average particle diameter of from about 0.1 microns to about 200 microns, and

(ii) 90 to 99.99 parts by weight of a transparent thermoplastic polymer,

wherein the polymer product exhibits an average translucency having a contrast ratio of about 2% to about 60% higher than the contrast ratio of a polymeric part comprising the polymer alone, at a molded part thickness of 0.030 inches.

17. The polymeric product of claim 16, wherein the particulate material comprises an average particle diameter of from about 1 micron to about 100 microns.

18. The polymeric product of claim 16, wherein the particulate material is selected from the group consisting essentially of calcium carbonates, calcium sulfates, talc, silicates, kaolin, silicas, mica flakes, mica platelets, mica pearls, titanates, metal sulfates, metal carbonates, sulfides, metal oxides, borides, wollastonite, basalt, boron, ceramics, single crystal fibers, organic flatting agents, acrylic flatting agents, fiber organic resins, ground organic resins, and mixtures thereof.

19. The polymeric product of claim 16, wherein the polymer is selected from the group of transparent and near transparent grades of thermoplastic polymers consisting essentially of polyolefins, polyethylene terephthalate, glycol-modified polyethylene terephthalate, glycol-modified polycyclo-hexanemethanol terephthalate, acid-modified polycyclo-hexanemethanol terephthalate, polystyrene, styrene acrylonitrile copolymers, styrene butadiene, styrene acrylic ester, acrylonitrile butadiene styrene, acrylo-nitrile styrene acrylic ester, acrylics, polymethacrylo-nitrile, ethylene methylacrylate, polymethylmethacrylate, ethylene ethylacrylate, ethylene butylacrylate,

ethylene acrylic ester, cellulose butyrate, polymethylpentene, polyisobutene, polybutene, polyamides, polycarbonate, ionomers, polyurethane, liquid crystal polymers, cellulose propionate, polyvinyl alcohol, ethylene vinyl alcohol, ethylene vinylacetate copolymer, polyvinyl chloride, high density polyethylene, polypropylene, polyacetal, and copolymers, grafts and blends thereof.

20. A method for imparting a translucent optical effect to a transparent thermoplastic polymer, comprising the steps of:

a) forming a substantially homogeneous mixture comprising (i) 0.01 to 10 parts by weight of a particulate, light-scattering material having an average particle diameter of from about 0.1 microns to about 200 microns, and (ii) 90 to 99.99 parts by weight of a transparent thermoplastic polymer; and

b) molding, extruding or forming the homogeneous mixture to form a translucent molded, extruded or formed polymer product, wherein, after curing, the polymer product exhibits an average translucency as measured by a contrast ratio of about 2% to about 60% higher than the contrast ratio of a polymer part comprising the polymer alone, at a molded part thickness of 0.030 inches.

21. A method for imparting a translucent optical effect to a transparent thermoplastic polymer, comprising the steps of:

a) forming a substantially homogeneous concentrate mixture comprising (i) 40 to 90 parts by weight of a finely ground, finely flaked or finely pelletized carrier agent selected from the group consisting essentially of a first transparent thermoplastic polymer, a dispersing agent, and mixtures thereof, wherein the dispersing agent is selected from the group consisting essentially of silicone waxes, fatty acids, metallic salts, ionomer waxes, amide waxes, hydroxy stearates, olefinic

waxes, and mixtures thereof, and (ii) 10 to 60 parts by weight of a particulate, light-scattering material having an average particle diameter of from about 0.1 microns to about 200 microns;

b) forming a mixture that comprises 0.1 to 10 parts by weight of the concentrate and 90 to 99.9 parts by weight of a second transparent thermoplastic polymer that is chemically compatible with the carrier agent;

c) molding, extruding or forming the mixture to form a translucent polymer product, wherein, after curing, the polymer product exhibits an average translucency as measured by a contrast ratio of about 2% to about 60% higher than the contrast ratio of a polymer part comprising the polymer alone, at a molded part thickness of 0.030 inches.

22. The method of claim 21, further comprising the step of extruding and pelletizing the concentrate prior to forming the mixture.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 98/11745

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C08K3/00 C08L101/00 C08J3/20 //(C08L101/00,101:00, 101:00)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C08K C08L C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 9312 Derwent Publications Ltd., London, GB; Class A14, AN 93-096862 XP002078148 & JP 05 039400 A (ASAHI CHEM IND CO LTD) , 19 February 1993 see abstract ---	1-22
X	DATABASE WPI Section Ch, Week 9721 Derwent Publications Ltd., London, GB; Class A60, AN 97-231251 XP002078149 & JP 09 071685 A (MARUO CALCIUM KK) , 18 March 1997 see abstract --- -/--	1-22

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
21 September 1998	05/10/1998

Name and mailing address of the ISA	Authorized officer
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Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 483 759 A (SZYCHER MICHAEL ET AL) 20 November 1984 see example 2	1-22
X	DE 43 26 521 A (BRIDGESTONE CORP) 17 February 1994 see column 4, line 68 - column 5, line 23 see examples 2,3 see claims 1-5	1-22
X	GB 1 595 426 A (BAYER AG) 12 August 1981 see examples 1,3-5 see claims 1-11	1-22
X	US 4 906 676 A (IDA KOZO) 6 March 1990 see claims 1-6	1-22

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 98/11745

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4483759 A	20-11-1984	AU 1647383 A	05-01-1984
		CA 1200647 A	11-02-1986
		CH 657863 A	30-09-1986
		DE 3323581 A	12-01-1984
		GB 2123012 A	25-01-1984
		JP 59020320 A	02-02-1984
		NL 8302335 A	01-02-1984
DE 4326521 A	17-02-1994	JP 6059105 A	04-03-1994
		JP 6059106 A	04-03-1994
		FR 2694641 A	11-02-1994
		US 5744534 A	28-04-1998
GB 1595426 A	12-08-1981	DE 2650340 A	11-05-1978
		FR 2370077 A	02-06-1978
		JP 53057244 A	24-05-1978
US 4906676 A	06-03-1990	JP 61069867 A	10-04-1986